ISSN 0031-918X, The Physics of Metals and Metallography, 2015, Vol. 116, No. 7, pp. 706–710. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.E. Barmin, O.V. Sobol', A.I. Zubkov, L.A. Mal'tseva, 2015, published in Fizika Metallov i Metallovedenie, 2015, Vol. 116, No. 7, pp. 745–749.

STRENGTH AND PLASTICITY

Modifying Effect of Tungsten on Vacuum Condensates of Iron

A. E. Barmin[a], O. V. Sobol'[a], A. I. Zubkov[a], and L. A. Mal'tseva[b]

[a] *National Technical University (Khar'kov Polytechnic Institute), ul. Frunze 21, Khar'kov, 61002 Ukraine*
[b] *Yeltsin Ural Federal University, ul. Mira 19, Ekaterinburg, 620002 Russia*
e-mail: axel.com.ua@gmail.com, mla44@mail.ru

Received September 25, 2014; in final form, January 28, 2015

Abstract—Laws of the structure formation, as well as the strength properties and thermal stability of vacuum condensates of the Fe–W system have been studied. It has been found that the alloying of iron foils with tungsten to 1 at % makes it possible to disperse the grained structure of the condensates to nanometric dimensionality and to markedly enhance their strength properties and recrystallization temperature. Thus, the foils containing ~0.8% tungsten and grains of about 50 nm in size exhibit the hardness 5.5 GPa and recrystallization temperature 800°C. These results can be used to devise compositions of the steels designed for subsequently obtaining high-strength and thermostable nanostructural states.

Keywords: vacuum condensates, modification, segregation, nanocrystallized materials

DOI: 10.1134/S0031918X15070017

INTRODUCTION

The efficient method of dispersing a grained structure of metals and alloys is modification of their melts with elements and substrates that adsorb on the surfaces of growing grains and prevent their growth upon crystallization. These adsorptive layers enhance the recrystallization temperature of the alloys produced and improve their strength properties. In addition, to date, rules and criteria for choosing modifier substances are unavailable, and laws of the formation and structures of these adsorptive layers have not been established. This is for to many reasons, one of which is the presence of impurities in melts that retard the interaction of modifier substances with the solidification front in the process of competitive adsorption.

Thermal deposition from the vapor phase in a vacuum onto nonorienting substrates of one-component metals with a controlled degree of purity and purposeful modification of their vapor flow with modifier substances make it possible to study the character of the interaction of these elements with the surface of growing crystals of the matrix metal and to minimize a masking effect of foreign elements.

In this connection the purpose of this work was to investigate the effect of tungsten on the structure formation, strength properties, and recrystallization temperature of vacuum condensates of iron.

EXPERIMENTAL

Fe–W condensates 10–30 μm thick were produced by the simultaneous electron-beam evaporation of the components in a vacuum of ~1.3×10^{-3} Pa and precipitation onto nonorienting glass-ceramic substrates in a temperature range of 250–550°C. The temperature was controlled by chromel–alumel thermocouples. The vacuum-remelted Fe and W of 99.99 wt % purity were used as initial materials for evaporation. The amount of alloying elements in condensates changed from 0.15 to 0.8 at % via variations in the precipitation rate of the components.

The elemental composition of condensates was studied by the method of X-ray fluorescence (XRF) analysis, and the elemental composition of local sections of the samples was determined using energy dispersive X-ray spectroscopy (EDS). Structural investigations were performed by transmission electron microscopy on PEM-100 and JEM-2100 microscopes and by X-ray diffractometry on a DRON-3M diffractometer. Electron-microscopic investigations were conducted on the samples thinned by jet electrolytic polishing on a PTF-2 device.

Mechanical properties were controlled by measuring microhardness on a PMT-3 device at a load of 10 g and with 7 s of holding. The load was selected so that the diagonal of an indentation was smaller than the sample thickness by a factor of 1.5.

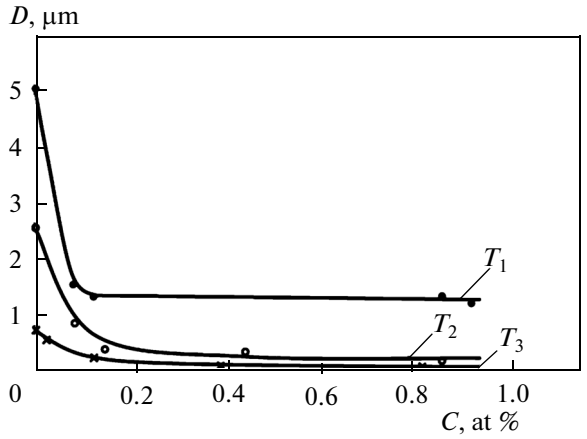

Fig. 1. Dependences of the average grain size on the tungsten concentration (the XRF method): $T_1 = 550°C$, $T_2 = 450°C$, and $T_3 = 250°C$.

RESULTS AND DISCUSSION

Figure 1 displays experimental dependences of the average grain size of the iron matrix (D) on the tungsten content (C) in condensates produced at different temperature of the substrate (T).

It can be seen that, even at a tungsten content of only 0.10%, the iron grain size decreases sharply, e.g., from 5 to 1.3 μm for T_1. When the tungsten concentration increases further, the experimental curves nearly reach saturation, and the minimum-attainable grain size (D_{min}) remains constant. A reduction in the temperature of the substrate does not change the behavior of $D = f(C)$ dependences and leads to a decrease in D_{min} to 0.3 μm and 50 nm for T_2 and T_3, respectively, and to an increase in the tungsten concentration (which corresponds to regions in which the behavior of the experimental curves changes) from 0.15 to 0.8 at %. For all of the studied samples, the crystal-lattice parameter remains constant and corresponds to the value characteristic of α-Fe. This result indicates the lack of solubility of tungsten in the crystal lattice of α-Fe condensates produced under the employed technological conditions [1].

Elemental analysis of local sections of Fe–W foils with an average tungsten content of 0.13 at % by the EDS method (Fig. 2) indicates that, when tungsten concentrations correspond to descending branches of $D = f(C)$ dependences, almost all tungsten is localized in the iron-grain boundaries. In this case, no second-phase particles were found in the structure.

At high tungsten concentrations, signs appear that indicate the presence of fine-dispersed second-phase particles in the region of grain boundaries of the iron matrix (Fig. 3).

These experimental results and data of [2] suggest that, upon the condensation of vapor mixtures of iron

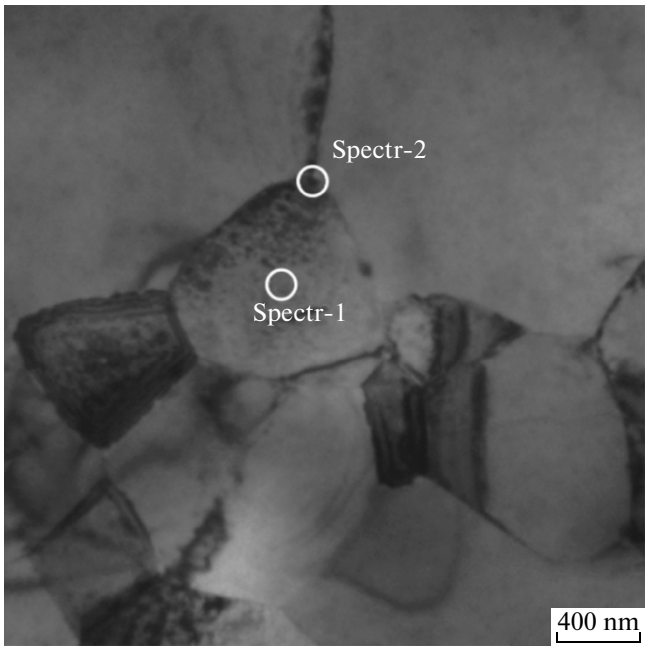

Fig. 2. Point elemental analysis by the EDS method in Fe–W foils (T_1, W ~ 0.15 at %): spectr-1, 0.03 at % W and spectr-2, 0.16 at % W.

with tungsten, the surface of growing grains of the iron matrix are enriched with tungsten and, at its specific content their growth stops and, correspondingly, $D = f(C)$ dependences reach saturation. These experimentally determined concentrations at temperatures T_1, T_2, and T_3 are 0.15, 0.35, and 0.8 at %, respectively.

These assumptions are supported by evaluting the tungsten concentrations needed to form a continuous monolayer at the surface of iron grains of minimum sizes (D_{min}).

Indeed, in the first approximation, if we take the shape of the iron-matrix grain to be a sphere with diameter D, V_m is the matrix-grain volume, V_b is the grain-boundary volume, V_t is the total volume, v_m is the atomic volume of the matrix grain, v_b is the atomic volume of the segregating-element atom, d_m is the matrix-atom diameter, N_m is the number of matrix atoms in the bulk of the grain, N_b is the number of segregating-element atoms in the monolayer, and f_b is the fraction of segregating-element atoms necessary to form the monolayer, we obtain

$$V_m = \frac{\pi D^3}{6}; \quad (1)$$

$$V_t = \frac{\pi(D + 2d_b)^3}{6} = \frac{\pi D^3}{6}\left(1 + \frac{2d_b}{D}\right)^3 \approx \frac{\pi D^3}{6}\left(1 + \frac{6d_b}{D}\right), \quad (2)$$

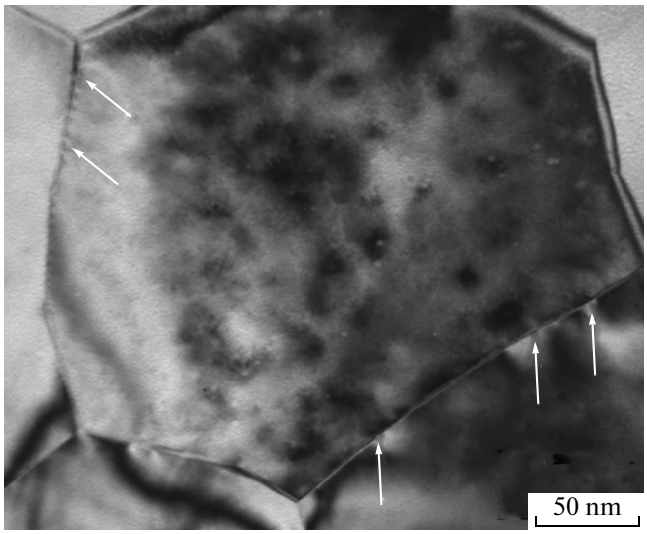

Fig. 3. Electron-microscopic bright-field image of the fine structure of Fe–W foils (T_1, W ~ 0.8 at %).

Because $\frac{d_b^3}{D^3}$ and $\frac{d_b^2}{D^2} \ll 1$,

$$V_b = V_t - V_m = \frac{\pi D^3}{6}\left(1 + \frac{6d_b}{D}\right) - \frac{\pi D^3}{6} = \pi D^2 d_b, \quad (3)$$

$$f_b = \frac{N_b}{N_b + N_m} = \frac{V_b/v_b}{V_b/v_b + V_m/v_m} = \frac{1}{1 + \frac{V_m v_b}{V_b v_m}} = \frac{1}{1 + \frac{\pi D^3 v_b}{6\pi D^2 d_b v_m}} = \frac{1}{1 + \frac{D d_b^2}{6 d_m^3}}. \quad (4)$$

The tungsten concentrations thus calculated are 0.1, 0.4, and 1.25 at % for minimum sizes of iron grains 1.3. 0.3, and 0.05 μm, respectively, which is in good agreement with the experimental data presented in Fig. 1.

These results indicate that, upon the condensation of Fe–W vapor mixture with a very low concentration of tungsten, its (W) atoms exhibit activity in relation to the surface of growing iron grains and, upon their contact, form grain-boundary segregations. In the literature, there are contradictory data on the tendency of tungsten to grain-boundary segregation. In metallurgical iron alloys, no enhancement in the tungsten concentration was usually observed in near-boundary regions, but the growth of microhardness in the near-boundary regions of α-Fe grains by 30–35% (compared to the volume) was detected in [3]. It should be noted that, in this work, samples of an Fe–W alloy were prepared using vacuum remelting in order to minimize the remaining impurities. The regime of final heat treatment was as follows: annealing at a temperature of 880°C for 4 h, cooling to 700°C, holding at the given temperature for 24 h, and cooling with a furnace at a rate of 50 K/h, which should provide an adequate diffusion path of the alloying element.

It is well known [4] that, upon metallurgical production of alloys based on iron, its permanent satellites are sulfur and phosphorus; these elements segregate at the surface and boundaries of grains, which is caused by the following factors:

1. Sulfur and phosphorus are surface-active substances in relation to iron, and they effectively reduce its surface energy [5].

2. Sulfur and phosphorus are low-soluble in α-Fe [6], and introduction of tungsten leads to an additional decrease in the solubility; thus, addition of 1 wt % W reduces the solubility of phosphorus in α-Fe twofold at 1000°C [7], which should result in growth in the degree of segregation of phosphorus.

3. Diffusion mobility of sulfur and phosphorus is higher than that of tungsten [8]; thus, the diffusion coefficient of sulfur at 700°C compared to tungsten is higher by a factor of ~10^3.

The evaluation of the amount of sulfur and phosphorus using expression (4) necessary to cover the grain surface with one monolayer indicates that for metallurgical alloys with grains 10–250 μm in size (i.e., of 10–1 grain-size grade) 0.012 wt % of sulfur or 0.011 wt % of phosphorus is enough. However, even in high-quality steels the content of sulfur and phosphorus is limited to 0.02 and 0.03 wt % [4]. Therefore, it can be assumed that in metallurgical iron-based alloys the formation of segregations of sulfur and phosphorus, as compared to tungsten segregations, will be most likely. In our case, upon the production of vacuum condensates, we minimize harmful impurities by using components of vacuum remelting. In doing so, the competing adsorption decreases to a significant extent.

A reduction in the grain size of condensates and the formation of grain-boundary tungsten segregations that appear to increase the cohesive strength of iron-grain boundaries [7] are responsible for a considerable enhancement in the strength properties of Fe–W condensates compared to both one-component Fe foils and Fe–W metallurgical alloys (Fig. 4). The presented data illustrate the effect of the tungsten content on the hardness of the Fe–W condensates produced at different temperatures of substrates, rates of evaporation and condensation, degree and purity of vacuum, etc. It can be seen that the hardness of iron condensates alloyed with tungsten at its content of about 1 at % exceeds the corresponding values for one-component iron samples nearly fivefold. Other strength characteristics grow analogously [12]. Note that this enhancement in the strength properties of Fe–W alloys of met-

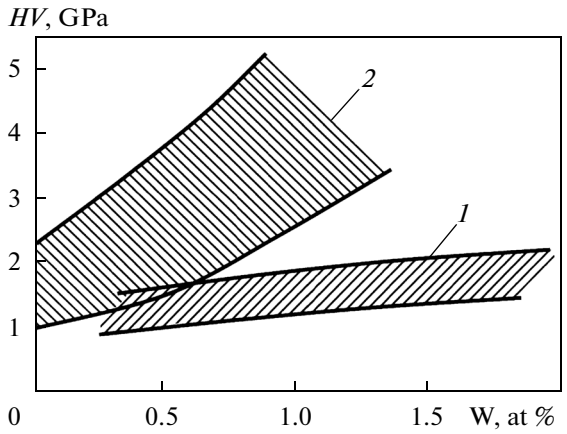

Fig. 4. Effect of the content of alloying element on the hardness of iron: (*1*) region of Fe–W alloys of metallurgical origin [9–11] and (*2*) region of Fe–W alloys produced by electron-beam evaporation and condensation in vacuum.

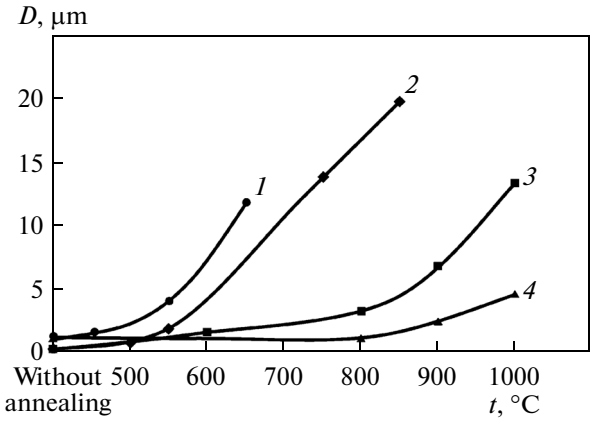

Fig. 5. Effect of the annealing temperature on the average grain size: (*1*) Steel 20 (mechanical–thermal treatment [13]); (*2*) submicrocrystalline armco iron ($e = 5.5$, $\tau = 1$ h) [14, 15]; (*3*) Fe condensate (T_3, $\tau = 0.5$ h); and (*4*) Fe–W condensate (T_1, W ~ 0.15 at %, $\tau = 0.5$ h).

allurgical origin occurs at a tungsten concentration of about 14 at %.

Growth of grains of the iron matrix (in whose volume second-phase particles are absent) in condensates with the tungsten content that corresponds to the inflection of $D = f(C)$ dependences (Fig. 1) occurs upon annealing at ~800°C, which exceeds the analogous temperature for some iron-based metallurgical alloys (Fig. 5). It can be assumed that this is connected with the retarding action of grain-boundary tungsten segregations whose monolayer character assumes tight bonding with iron atoms [16]. It should be noted that this appreciable difference in the behavior upon annealing of iron-based alloys with much the same grain size of the initial grained structure produced by different methods calls for a separate consideration.

CONCLUSIONS

(1) It was found that the addition of tungsten to 1 at % into a vapor flow of iron enables the grained structure of vacuum condensates to be dispersed to nanometric size level.

(2) Fe–W foils possess high strength properties. For example, their hardness at a tungsten content of ~0.8% is ~5.5 GPa, which is attained in Fe–W alloys of metallurgical origin at 14 at %.

(3) The grained structure of these materials is thermostable. Grain growth starts at ~800°C, which is higher by 250–300 K than the analogous temperature for some iron-based alloys with the same grain size of the initial grained structure.

(4) The experimental results and our estimates suggest that tungsten atoms upon condensation of two-component vapor of Fe–W adsorb on the surface of growing grains in the form of monolayers stopping their further growth. When grains come in contact in the process of condensate formation these adsorptive layers appear to form the grain-boundary tungsten segregations that yield a high thermal stability of the grained structure.

REFERENCES

1. A. E. Barmin, A. I. Zubkov, and A. I. Il'inskii, "Structural features of the vacuum condensates of iron alloyed with tungsten," Funct. Mater. **19**, 256–259 (2012).
2. A. E. Barmin, A. I. Il'inskii, and A. I. Zubkov, "Submicro- and nanocrystalline vacuum iron-based condensates (foils)," Nanosist., Nanomater., Nano-Tekhnol. **8**, 547–551 (2010).
3. M. Braunovic and C. W. Haworth, "On the phenomenon of grain-boundary hardening in iron," J. Mater. Sci., **9**, 809–820 (1974).
4. A. P. Gulyaev, *Metal Science* (Metallurgiya, Moscow, 1986) [in Russian].
5. Ya. E. Gol'dshtein and V. G. Mizin, *Modification and Microalloying of Cast Iron and Steel* (Metallurgiya, Moscow, 1986) [in Russian].
6. *Phase Diagrams of Binary Metallic Systems: A Handbook*, In 3 vols., Vol. 2, Ed. by N. P. Lyakishev, (Mashinostroenie, Moscow, 1996) [in Russian].
7. R. W. Cahn and P. Haasen, *Physical Metallurgy*, 4th Ed. (North-Holland, 1996), Vol. 2.
8. B. S. Bockshtein, *Diffusion in Metals* (Metallurgiya, Moscow, 1978) [in Russian].
9. A. E. Vol, *Structure and properties of Binary Metallic Systems* (Fizmatlit, Moscow, 1962), Vol. 2 [in Russian].

10. A. P. Gulyaev and E. F. Trusova, "Regularities of changes in the properties of solid solutions," Zh. Tekh. Fiz. **20**, 66–78 (1950).
11. I. Artinger, *Tool Steels and Their Heat Treatment* (Metallurgiya, Moscow, 1982) [in Russian].
12. A. I. Il'insky, A. E. Barmin, and S. I. Lyabuk, "Structure and strength characteristics of dispersion-hardened composite foils (films) based on iron and nickel," Funct. Mater. **20**, 477–484 (2013).
13. A. E. Barmin, "Formation and study of submicrocrystalline structure in low carbon steel," in *Vestn. Nat. Tekh. Univ. "Khar'k. Politekhn. Inst." Special issue: New Solutions in Modern Technologies* (NTU KhPI, Kharkov, 2007), no. 30, pp. 48–52 [in Russian].
14. L. M. Voronova, M. V. Degtyarev, and T. I. Chashchukhina, "Low-temperature recrystallization of submicrocrystalline structure of Armco iron and 30G2R steel," Phys. Met. Metallogr. **98**, 83–91 (2004).
15. M. V. Degtyarev, L. M. Voronova, and T. I. Chashchukhina, "Grain growth upon annealing of Armco iron with various ultrafine-grained structures produced by high-pressure torsion deformation," Phys. Met. Metallogr. **99**, 276–285 (2005).
16. A. Zangwill, *Physics of Surfaces* (Cambridge University Press, Cambridge, 1988; Mir, Moscow, 1990).

Translated by I Krasnov